

# PATENT SPECIFICATION

NO DRAWINGS

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International Classification:—B01j. C07d, f. (A23k, l. C08c, d, g. C10g, m. C11b).

## COMPLETE SPECIFICATION

### Antioxidant Compositions

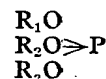
We, ETHYL CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 100 Park Avenue, New York 17, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to synergistic additives to protect organic material from deterioration. Organic compositions including hydrocarbon fuels, lubricants and polymers are all subject to oxidative deterioration at elevated temperatures or upon prolonged exposure to the elements. In polymeric compositions, including natural rubber and polyethylene, oxidative deterioration causes the loss of desirable characteristics as well as an increase in weight. Hydrocarbon fuel compositions are deteriorated by oxygen during storage to form undesirable components in the fuel.

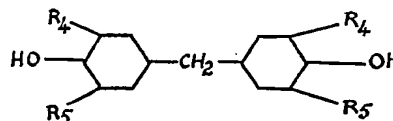
Industrial and engine lubricants—e.g., mineral oils and synthetic diester oils—undergo oxidative deterioration in service, particularly at elevated temperatures. Resulting from this deterioration are the formation of gums and sludges, the corrosion of metal parts of the equipment with which the oils are used, the loss of lubricating properties of the oil, and the like. Shortcomings of prior antioxidants include low effectiveness except at high concentration, low solubility in the oil, high cost, and difficulty of preparation. Furthermore, most prior art antioxidants possess marginal effectiveness when the oils are subjected to drastic oxidizing conditions, such as are encountered when the oils are held at elevated temperatures, agitated with air, and contain in

suspension iron and other metal oxides which catalyze the decomposition of the oil.

According to the invention we provide a synergistic antioxidant mixture for addition to organic material subject to oxidative deterioration comprising a phosphite ester having the formula



wherein  $R_1$  and  $R_2$  are alkyl, alkoxyalkyl, haloalkyl, cyclalkyl, halocyclalkyl, aralkyl, aryl, alkaryl, haloaryl or haloalkaryl radicals and  $R_3$  is one of the aforementioned radicals or hydrogen; and a methylene bis-phenol having the formula



wherein  $R_1$  is an alkyl group which contains from 3 to 12 carbon atoms and is branched on its alpha carbon atom and  $R_2$  is an alkyl group containing from 1 to 12 carbon atoms in amount such that there is from 0.005 to 1000 parts by weight of said phenyl per part of phosphite. Our additives markedly enhance the resistance of engine and industrial oils against oxidative deterioration, especially under the foregoing drastic conditions. The additives further effectively inhibit the oxidative deterioration of lubricating oil. Organic polymers, particularly polypropylene, can be stabilized against oxidative deterioration and discoloration by the presence therein of a small quantity of our antioxidant mixture. The

mixture can be used to improve antiknock fluids and stabilize edible material.

We provide organic compositions tending to deteriorate in the presence of air, oxygen or ozone, protected by an antioxidant quantity of our synergistic mixture consisting of from 0.025 to 4—and preferably 0.1 to 1—per cent by weight based on the material to be protected of the oil-soluble phosphite ester; and from 0.01 to 5—preferably 0.25 to 2—per cent by weight of a methylene bis phenol.

The phosphorus compounds preferably contain a total of up to about 24 carbon atoms and, when the compounds are halogen substituted, it is preferable that there be no more than 3 halogen atoms in the molecule. These halogens are preferably chlorine or bromine, chlorine being the best, although they can be fluorine or iodine. Especially preferred are dialkyl hydrogen phosphites in which the alkyl groups each contain up to 12 carbon atoms. These compounds gave synergistic effects, particularly when combined with 4,4'-methylenebis-(2,6-diisopropyl phenol) or 4,4'-methylenebis-(6-*tert*-butyl-*o*-cresol).

Our stabilized compositions possess unexpectedly great resistance against oxidative deterioration, resulting from the presence of the specified additives. It has been found from actual tests that lubricants containing the synergistic additives have their useful lives prolonged by well over 1800 times.

The phosphites used are either neutral phosphite ester ( $R_3$  of the above formula is not hydrogen) or diesterified hydrogen phosphites ( $R_3$  is hydrogen) which are also called phosphonates. Dialkyl hydrogen phosphites, such as diisopropyl hydrogen phosphite, di-*tert*-butyl hydrogen phosphite, dioctyl hydrogen phosphite, and di-(2,6-dimethylheptyl) hydrogen phosphite, where the alkyls each contain up to about 12 carbon atoms are preferred. When the methylenebis phenol is 4,4'-methylenebis-(2,6-di-*tert*-butyl phenol), best results occur when the alkyl groups of the dialkyl hydrogen phosphite each contain from 4 to 12 carbon atoms. On the other hand, when the phenolic compounds 4,4'-methylenebis(2,6-diisopropyl phenol) and 4,4'-methylenebis(6-*tert*-butyl-*o*-cresol) are used, best results are obtained from dialkyl hydrogen phosphites in which the alkyl groups each contain from 1 to 8 carbon atoms.

The phosphorus esters are reasonably effective antioxidants under mildly oxidizing conditions. However, their effectiveness falls off sharply at elevated temperatures, especially in the presence of iron oxides. It is thus remarkable that when these materials are combined with the particular bis-phenols described herein, such powerful synergistic effects are achieved even under these drastic conditions.

The preferred phosphite esters for use in our compositions are the hydrogen phosphites, or phosphonates, as it has been found that an

extremely high degree of synergism is obtained by their use.

We prefer the use of 4,4'-methylenebis(2,6-dialkylphenol) compounds in which the groups represented by  $R_1$  in the above formula are *tert*-alkyl groups containing from 4 to 8 carbon atoms. These compounds are particularly effective in conjunction with the above phosphorus esters or antioxidants for oxygen-sensitive oils, such as lubricating oil, transformer oil, turbine oil, gear oil, and greases containing the aforesaid type of oils.

We particularly prefer the use of a 4,4'-methylenebis(2-methyl-6-*tert*-alkylphenol). These compounds in conjunction with a phosphite give rise to excellent antioxidant mixtures for a wide variety of oxygen-sensitive organic material, particularly oils and greases of the type described above as well as antiknock fluids, polymers and fatty material.

The phenolic compounds used are white crystalline solids and are soluble in various organic solvents and in gasolines, diesel fuels and hydrocarbon oils. These compounds are further characterized by being relatively stable, non-hygroscopic, readily crystallizable materials.

Thus we provide a lubricating oil composition containing a synergistic mixture consisting of from 0.025 to 4 per cent by weight based on the oil of a dialkyl hydrogen phosphite in which each alkyl group contains from 1 to 8 carbon atoms and from 0.1 to 3 per cent by weight based on the oil of 4,4'-methylenebis-(2,6-diisopropyl phenol) or 4,4'-methylenebis-(6-*tert*-butyl-*o*-cresol).

We also provide a lubricating composition containing a synergistic mixture consisting of from 0.025 to 4 per cent by weight based on the oil of a dialkyl hydrogen phosphite in which each alkyl group contains from 4 to 12 carbon atoms and from 0.1 to 3 per cent by weight based on the oil of 4,4'-methylenebis-(2,6-di-*tert*-butyl phenol).

The structure of the bis-phenols is very important. The synergistic effects appear to be tied in, in some inexplicable manner, with the configuration, chain length and relative positions of the alkyl groups and the relative positions of the methylene bridge and the hydroxyl groups. This is borne out by tests showing that departures from the above specific structural criteria of the bis-phenols result not only in loss of synergistic effect, but in a sharp drop in over-all effectiveness even when other phenolic compounds are used with the preferred phosphorus additives. For example, inferior results have been achieved by combining 4-methyl-2,6-di-*tert*-butyl phenol with dialkyl hydrogen phosphites. Why this should be the case is a question which presently cannot be answered, especially since 4-methyl-2,6-di-*tert*-butyl phenol is a standard, commercially used and generally effective antioxidant.

Our additives are useful as antioxidants in

a wide variety of oxygen-sensitive materials; thus, liquid and solid products derived from petroleum crude are found to possess greatly increased storage stability by the use of our antioxidants. For example, gasoline, jet fuel, kerosene, fuel oil, turbine oils, insulating oils, motor oils and various waxes have increased oxidative stability when they contain one of our antioxidant mixtures. Likewise, liquid hydrocarbon fuels which contain organometallic additives such as tetraethyllead and other organometallic compositions which are used as fuel additives attain appreciably increased oxidative stability by the practice of this invention. Furthermore, fuels which contain halogen and phosphorus-containing scavengers for these organometallic compounds are improved. In addition to increased storage stability, lubricating oils and functional fluids, such as automatic transmission and hydraulic fluids, both those derived from naturally occurring hydrocarbons and those synthetically prepared, achieve a high degree of resistance to oxidation during use at elevated temperatures. It has been found that lubricating oils may be employed at extremely high temperatures without undergoing oxidative degradation when protected by one of our antioxidants. The addition of small quantities of our compositions to such materials as hydraulic, transformer and other highly refined industrial oils as well as crankcase lubricating oils and lubricating greases prepared from these oils by the addition of metallic soaps, greatly increase their resistance to deterioration in the presence of air, oxygen or ozone. Furthermore, organic soaps used in the preparation of lubricating greases are themselves stabilized.

Organometallic compositions such as tetraethyllead and tetraethyllead antiknock fluids containing halohydrocarbon scavengers, dyes and which may contain various phosphorus compounds and other organometallic additives are stabilized against deterioration during storage by the addition thereto of one of our antioxidant compositions.

Our compositions are also extremely effective antioxidants for elastomers including high molecular weight unsaturated hydrocarbon polymers both derived from naturally occurring sources and those synthetically prepared. Thus, natural rubbers and synthetic rubbers, including oil extended rubbers and sulfur vulcanized rubbers are greatly improved. Examples of the synthetic rubbers protected by the practice of this invention include such synthetics as polybutadiene, methyl rubber, polybutadiene rubber, butyl rubber GR—S rubber, GR—N rubber, picroylene rubber and dimethylbutadiene rubber.

We can also protect petroleum waxes against the oxidative deterioration which leads to rancidity. Furthermore, our compositions are extremely useful in stabilizing fats and oils of animal or vegetable origin which become

rancid during periods of storage due to oxidative deterioration. Typical animal fats thus benefited include butter fat, lard, beef, tallow, fish oils—such as cod liver oil—as well as various foods containing or prepared in animal fats which tend to deteriorate. These include, for example, potato chips, fried fish, donuts, crackers, and various types of pastry such as cakes and cookies. Furthermore, fat fortified animal feeds and fish meals used as animal feeds are greatly benefited. Not only are these compositions protected against oxidative deterioration but the inclusion of our compositions in such materials inhibits the degradation of vitamins A, D and E and certain of the B complex vitamins. Examples of compositions containing oils derived from vegetable sources which are benefited include castor oil, soy bean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, citrus oils, cotton seed oil and various compositions containing these including peanut butter, peanuts and other whole nuts, salad dressings, margarine and other vegetable shortenings.

Our compositions are also useful antioxidants for various organic compounds and polymeric materials including polystyrene, polyvinylchloride, polyvinyl acetate, various epoxide resins and polyester resins and polymers including the alkyds. However, in particular our compositions are outstanding antioxidants for saturated hydrocarbon synthetic polymers derived from polymerization of an aliphatic monoolefin hydrocarbon compound having preferably up to 5 carbon atoms and only a single unit of unsaturation per monomeric molecule. Examples of such monomers include ethylene, propylene, butylene, isobutylene, 2-methyl-4-butene, 2-methyl-3-butene and the like. Thus, the polymers are homopolymers and copolymers of ethylene, propylene, butylene, isobutylene and the pentenes and are usually solid.

A preferred embodiment of the invention involves the provision of lubricating oil containing a small antioxidant quantity of 4,4'-methylenebis(2,6-dialkylphenol). It has been found in actual practice that small amounts of these mixtures very effectively stabilize lubricant compositions—e.g. petroleum hydrocarbon oils and synthetic diester oils—against oxidative deterioration.

The unexpected and disproportionately increased antioxidant effects show up under normal conditions encountered in the manufacture, shipment, storage and use of lubricants. It is especially significant that the synergism is very pronounced under high-temperature oxidizing conditions since there is a real need for lubricants that are stable under these conditions. Moreover, these synergistic effects are undaunted by the presence in the oil of deleterious oxidation catalysts, such as iron oxide, which at high temperatures norm-

ally promote catastrophic deterioration of lubricants.

5 In formulating the lubricants, the above synergistic additives are blended in appropriate quantity with the oil, the phosphite and the bis-phenol being used either as a pre-formed blend or mixture, or by adding them separately in either order.

The following examples illustrate various specific embodiments. Parts and percentages are by weight. The physical characteristics of the illustrative oils used in Examples 1 through 9 are shown in Table I. 10

TABLE I  
Properties of Representative Petroleum Hydrocarbon Oils

Oil:	A	B	C	D	E	F
Gravity at 60° API	30.3	30.5	28.8	31.1	20.5	31.0
Viscosity, Saybolt						
Seconds at 100° F.	178.8	373.8	309.8	169.0	249.4	335.4
Seconds at 210° F.	52.0	58.4	63.8	51.5	45.7	68.4
Viscosity Index	154.2	107.4	141.9	157.8	35.8	144.4
Pour Point	-30	+10	-20	-15	—	0
Flash Point	410	465	—	—	365	385
Sulfur, per cent	0.2	0.3	0.3	0.3	0.3	0.1

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## EXAMPLE 1

To 100,000 parts of Oil A is added with stirring 25 parts (0.025 per cent) of trimethyl phosphite. To this oil is then added 100 parts (0.1 per cent) of 4,4'-methylene-bis(2,6-di-(2-dodecyl) phenol). The resultant oil possesses greatly enhanced resistance to oxidative deterioration.

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## EXAMPLE 2

25 To 100,000 parts of Oil B are added 3000 parts (3 per cent) of trixylyl phosphite and 200 parts (0.2 per cent) of 4,4'-methylenebis-(6-isopropyl-*o*-cresol). After mixing, the resulting oil possesses greatly enhanced oxidation resistance.

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## EXAMPLE 3

35 With 100,000 parts of Oil C are blended 500 parts (0.5 per cent) of dibutyl hydrogen phosphite and 500 parts (0.5 per cent) of 4,4'-methylenebis(2,6-di-*tert*-butyl phenol). The resulting oil is found to possess markedly great resistance to oxidative deterioration.

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## EXAMPLE 4

45 To 100,000 parts of Oil D are added 1000 parts (1 per cent) of dibenzyl hydrogen phosphite and 2000 parts (2 per cent) of 4,4'-methylenebis(2-nonyl-6-*tert*-butyl phenol). After agitation, the homogeneous lubricant possesses great resistance against oxidative deterioration.

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## EXAMPLE 5

With 100,000 parts of Oil E are blended 80 parts (0.08 per cent) of tri-(3-bromooctyl) phosphite and 800 parts (0.8 per cent) of 4,4'-methylenebis(2-ethyl-6-(1,1,3,3-tetramethylbutyl) phenol). The resulting lubricant is found to possess great resistance to high-temperature oxidative deterioration.

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## EXAMPLE 6

To 100,000 parts of Oil F are added 4000 parts (4 per cent) of dicumenyl hydrogen phosphite and 3000 parts (3 per cent) of 4,4'-methylenebis(6-*tert*-amyl-*o*-cresol). After mixing, the resultant oil is greatly resistant to oxidative deterioration.

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## EXAMPLE 7

With 100,000 parts of Oil A are blended 50 parts (0.05 per cent) of tri-(2-ethoxyethyl) phosphite and 500 parts (0.5 per cent) of 4,4'-methylenebis(2-isopropyl-6-decyl phenol). Greatly increased is the resistance of this oil against oxidative deterioration.

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## EXAMPLE 8

To 100,000 parts of Oil B are added 100 parts (0.1 per cent) of butyl decyl hydrogen phosphite and 250 parts (0.25 per cent) of 4,4'-methylenebis(6-*tert*-butyl-*o*-cresol). The mixture is agitated and found to possess extreme resistance against oxidative deterioration.

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## EXAMPLE 9

5 To 100,000 parts of Oil C are added 500 parts (0.5 per cent) of tri-(4-chlorophenyl) phosphite and 200 parts (0.2 per cent) of 4,4'-methylenebis(2,6 - di(2 - hexyl) phenol). The finished oil is very highly resistant to oxidative deterioration.

10 In all of the foregoing illustrative examples, the increased resistance to oxidative deterioration results from a very substantial synergistic co-action of the additive combinations.

## EXAMPLE 10

15 To illustrate the synergistic effect a standard oil oxidation test was used. The equipment and test procedure as described by Kroger *et al*, Erdol and Kohle, 2, 389 (1949) served as the basis of the following tests. The equipment and procedure were slightly modified in order to make the oxidizing conditions even more strenuous. In this manner, the test lubricants were subjected to exceedingly severe oxidizing conditions in order to establish conclusively the effectiveness of the additives under very adverse conditions. Furthermore, 25 the modifications were found to provide results which correlated extremely well with the test results of other standard procedures, including actual engine tests.

30 The equipment consists of a reaction cell connected with an open end monometer

whereby the total uptake of oxygen by the oil can be obtained by noting the drop in mercury in the monometer. Thus, the test oil sample is placed in the reaction cell which is flushed with oxygen and the temperature raised to 300°F. and held there until the substrate oil undergoes catastrophic oxidation as shown by the rapid uptake of oxygen. In all cases, the substrate oil was deliberately contaminated with iron hexoate as an oxidation promoter (0.05 weight per cent of iron as  $Fe_2O_3$  per 100 grams of oil). By so doing, a very close simulation of stringent oxidizing conditions prevailing with many uses of lubricants was achieved.

In the following tests, the oxidation stability of the test lubricant was determined by measuring its induction period, that is, the time required for catastrophic deterioration to occur under the foregoing conditions. Hence, the longer the induction time, the more stable was the lubricant.

In one series of tests, the base lubricant was a commercially available, additive-free mineral oil having a viscosity index of 106.5. Tested separately and in combination were 0.13 per cent by weight of dimethyl hydrogen phosphite and 0.42 per cent by weight of 4,4'-methylene - bis(2,6 - diisopropyl phenol). The phenomenal synergistic data are shown in Table II.

TABLE II

Effect of Additives on Lubricating Oil

Additive	Induction Time, min.	
	Calculated	Found
4,4'-Methylenebis(2,6-diisopropyl phenol)	—	43
Dimethyl hydrogen phosphite	—	3
4,4'-Methylenebis(2,6-diisopropyl phenol) + dimethyl hydrogen phosphite	46	1896

65 When these tests are repeated using di-(butoxyethyl) hydrogen phosphite or ditolyl hydrogen phosphite in place of dimethyl hydrogen phosphite, similar unexpected synergistic effects are noted, although the magnitude is not quite as large.

## EXAMPLE 11

70 In another example, dimethyl hydrogen phosphite (0.12 per cent) and 4,4'-methylenebis(6-*tert*-butyl-*o*-cresol) (0.42 per cent) were tested in the oil separately and in combination. The amazing synergistic data showing an exponentially lengthened induction time are presented in Table III.

TABLE III

Effect of Additives on Lubricating Oil

Additive	Induction Time, min.	
	Calculated	Found
4,4 <sup>1</sup> -Methylenebis(6- <i>tert</i> -butyl- <i>o</i> -cresol)	—	157
Dimethyl hydrogen phosphite	—	3
4,4 <sup>1</sup> -Methylenebis(6- <i>tert</i> -butyl- <i>o</i> -cresol) + dimethyl hydrogen phosphite	160	2885

Similar synergistic effects are found when the above tests are repeated using tripropyl phosphite, tri-(4-*tert*-butylbenzyl) phosphite, and dimethyl phenyl phosphite in place of the dimethyl hydrogen phosphite. Other bisphenols described herein also give very good synergistic effects when used in place of 4,4<sup>1</sup>-methylenebis(6-*tert*-butyl-*o*-cresol).

The great importance of the structure of the phenolic compound used in this invention was clearly shown by comparative tests. For example, the combination of 0.16 per cent of dimethyl hydrogen phosphite and 0.25 per cent of 4-methyl-2,6-di-*tert*-butyl phenol gave an induction time of only 118 minutes. Obviously, this value is infinitesimally small as compared to the phenomenal results characterizing this invention.

## EXAMPLE 12

To still further demonstrate the impressive results of our invention, many standard Polyveriform oxidation stability tests were carried out. References in the literature to this test are Ind. and Eng. Chem., Anal. Ed., 17, 302

(1945) and Anal. Chem. 21, 737 (1949). Tested was an initially additive-free 95 VI solvent-refined SAE 10 crankcase oil. The principal test conditions consisted of passing 70 liters of air per hour through the test oil for a total period of 20 hours while keeping the oil at 300°F. The oil was deliberately contaminated with iron hexoate as described above. Measurements made on the used oils showed the extent by which deterioration had occurred, or had been suppressed by an additive complement of this invention. The criteria were the acid number (the lower the acid number, the less the oil had deteriorated) and the per cent viscosity increase measured at 100°F. as compared with the viscosity of the new oil (the lower the per cent viscosity increase, the more stable was the lubricant).

In one series of Polyveriform tests, the additives tested separately and in combination were 1 per cent of 4,4<sup>1</sup>-methylenebis(2,6-di-*tert*-butyl phenol) and 0.16 per cent of di-*sec*-butyl hydrogen phosphite. The tremendous synergism is shown by the data in Table IV.

TABLE IV

Effect of Additives on Lubricating Oil

Additive	Acid Number	Per Cent Viscosity increase, SUS* at 100° F.
4,4 <sup>1</sup> -Methylenebis(2,6-di- <i>tert</i> -butyl phenol)	3.5	58
Di- <i>sec</i> -butyl hydrogen phosphite	2.7	33
4,4 <sup>1</sup> -Methylenebis(2,6-di- <i>tert</i> -butyl phenol) + di- <i>sec</i> -butyl hydrogen phosphite	0.7	9

\* Saybolt Universal Seconds

5 Besides being virtually unchanged as shown by the exceedingly low acid number and viscosity change, the tested oil showed absolutely no visual evidences of oxidative deterioration. The tested oil was given a perfect rating, showing that it looked the same as the original oil.

## EXAMPLE 13

10 In another series of Polyveriform tests, the additives were 1 per cent of 4,4'-methylenebis-(2,6-di-*tert*-butyl phenol) and 0.21 per cent of di(1,3-dimethylbutyl) hydrogen phosphite. The tremendous synergism provided by this mixture is shown by the data in Table V.

TABLE V

Effect of Additives on Lubricating Oil

Additive	Acid Number	Per Cent Viscosity Increase, SUS at 100° F.
4,4'-Methylenebis(2,6-di- <i>tert</i> -butyl phenol)	3.5	58
Di-(1,3-dimethylbutyl) hydrogen phosphite	4.3	56
4,4'-Methylenebis(2,6-di- <i>tert</i> -butyl phenol) + di-(1,3-di-methylbutyl) hydrogen phosphite	1.6	17

Here again the oil used was given a perfect visual rating.

## EXAMPLE 14

In still another series of tests, the additives were 4,4' - methylenebis(2,6 - di - *tert* - butyl phenol) (1 per cent) and dioctyl hydrogen

phosphite (0.25 per cent). The enormously increased resistance to oxidative deterioration of this lubricant of the invention is shown by the data in Table VI.

TABLE VI

Effect of Additives on Lubricating Oil

Additive	Acid Number	Per Cent Viscosity Increase, SUS at 100° F.
4,4'-Methylenebis(2,6-di- <i>tert</i> -butyl phenol)	3.5	58
Dioctyl hydrogen phosphite	6.4	140
4,4'-Methylenebis(2,6-di- <i>tert</i> -butyl phenol) + di-octyl hydrogen phosphite	1.5	10

As before, the oil used was given a perfect visual rating.

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## EXAMPLE 15

30 The synergistic effects persist in the presence of other commonly-used oil additives. This was shown by another series of Polyveriform tests in which the base mineral oil always contained 4 per cent by weight of a barium sulfonate detergent. The test conditions were as described above with the exception that copper-lead bearings were

35 immersed in the oils throughout the test period, so as to measure the extent by which the bearing metals were corroded during these stringent oxidizing conditions. Tested in this barium sulfonate-containing oil were 0.52 per cent of tri-(2-chloroisopropyl) phosphite plus 1 per cent of 4,4'-methylenebis(2,6-di-*tert*-butyl phenol) and 0.26 per cent of tri-(2-chloroisopropyl) phosphite plus 1 per cent of 4,4'-

methylenebis(2,6-di-*tert*-butyl phenol). A control sample of the barium sulfonate oil contained 0.52 per cent of tri-(2-chloroisopropyl)

phosphite in the absence of the bis-phenol. The striking results are shown in Table VII.

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TABLE VII  
Effect of Additives on Lubricating Oil

Additive	Bearing Weight, Loss, mg.	Acid Number	Per Cent Viscosity Increase, SUS at 100° F.
Tri-(2-chloroisopropyl) phosphite (0.52 per cent)	139.8	5.7	104
Tri-(2-chloroisopropyl) phosphite (0.52 per cent) + 4,4'-methylenebis(2,6-di- <i>tert</i> -butyl phenol) (1 per cent)	21.2	0.8	7
Tri-(2-chloroisopropyl) phosphite (0.26 per cent) + 4,4'-methylenebis(2,6-di- <i>tert</i> -butyl phenol) (1 per cent)	37.1	1.0	8

10 It is seen from the above data that not only are our compositions markedly synergistic in antioxidant effectiveness, but are surprisingly effective in minimizing bearing corrosion even when the phosphorus compound contains normally corrosive chlorine atoms.

#### EXAMPLE 16

15 The benefits of this invention are still further demonstrated by carrying out engine tests, such as the CRC L-38 Test, as described in "Development of Research Technique for Study of the Oxidation Characteristics of Crankcase Oils in the CLR oil Test  
20 Engine" published by the Coordinating Re-

search Council, New York, March, 1957. This test very effectively evaluates the oxidation and copper-lead bearing corrosion characteristics of engine crankcase oils. The technique involves operating the CLR Oil Test Engine under constant speed, air/fuel ratio, and fuel-flow conditions for a total of 40 hours, subsequent to a break-in period of 4.5 hours. Prior to each test, the engine is cleaned, pertinent measurements of engine parts are taken and a complete set of new piston rings and new copper-lead connecting-rod test bearing inserts are installed. The chief operating conditions are:

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Speed	3150 ± 25 rpm
Fuel-flow	4.5 to 5.0 lb/hr.
Air/fuel ratio	14.0 ± 0.5
Intake-air temperature	80° F., min.
Jacket-outlet coolant temperature	200° ± 2° F.
Spark advance	35° ± 1° btdc
Oil pressure	40 ± 2 psi
Crankcase vacuum	2 ± 0.5 in. water
Exhaust back pressure	0 to 1 in. mercury



Performance of the oil is judged by visual examination of the engine for deposits, by the weight loss of the test bearing and by comparison of inspection data on used oil samples with the inspection data on the new oil. When a typical additive-free, lubricating oil, such as any of those described in Table I, is subjected to this test, it is found that there has been a substantial weight loss of the test bearings and a considerable amount of deterioration of the oil. However, repetition of the test with the sole variable being that the oil is treated with an appropriate concentration of mixtures of phosphites and bis-phenols of this invention shows that on completion of the test, there has been a substantial reduction in the weight loss of the test bearings and that the used oil has been virtually unaffected.

Our additives very effectively stabilize such lubricating and industrial oils as crankcase lubricating oils, transformer oils, turbine oils, transmission fluids, cutting oils, gear oils, industrial oils, mineral white oils, glass annealing oils, oils thickened with soaps and inorganic thickening agents (grease), and, in general, engine and industrial oils that are normally susceptible to deterioration in the presence of air, particularly at elevated temperatures and most particularly in the presence of iron oxide.

Synergistic effects are exhibited when the above combination of additives are present in the concentration ranges described above. However, it has been further found that the greatest amount of synergism occurs when the phosphite and the bisphenol are present in certain relative proportions within the range of the foregoing concentrations. Thus, we particularly prefer lubricant compositions in which the phosphite and bisphenol are present in relative proportions such that there are from 0.5 to 5 moles of the phosphite per mole of bis-phenol.

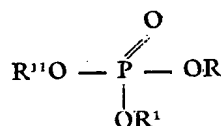
Our additive compositions are also useful as additives to functional fluids and automatic transmission fluids. The primary constituent of a functional fluid is a refined mineral lubricating oil having carefully selected minimum viscosity of 49 Saybolt Universal Seconds (SUS) at 210°F. and a maximum viscosity of 7,000 SUS at 0°F., generally a distillate oil, lighter than an SAE 10 motor oil. The oil usually amounts to between about 73.5 to about 97.5 per cent by weight of the finished fluid. Preferably, the base oil is selected from a paraffin base distillate such as a Pennsylvania crude.

The synthetic lubricants which are improved are, in general, non-hydrocarbon organic composition; i.e. organic compositions which contain elements other than carbon and hydrogen. Examples of general classes of material which can be protected against oxidative deterioration include diester lubricants, silicones, halogen containing organic compounds including the fluorocarbons, polyalkylene glycol lubricants, and organic phosphates which are suit-

able as hydraulic fluids and lubricants. The synthetic diester oils include sebacates, adipates, and so on, which find particular use as aircraft instrument oils, hydraulic and damping fluids, and precision bearing lubricants. These diester oils are exceedingly difficult to stabilize under high temperature conditions.

Another class of synthetic lubricants which achieve enhanced oxidative stability includes the "silicone" lubricants. The term "silicone" may be defined as a synthetic compound containing silicon and organic groups.

Another important class of synthetic materials which are improved are phosphate esters which are, in general, prepared by the reaction of an organic alcohol with phosphoric acid and have the general formula:



where R, R<sup>1</sup> and R<sup>11</sup> represent either hydrogen or an organic radical and where at least one of the groups represented by R, R<sup>1</sup> and R<sup>11</sup> is an organic radical. Typical of these material is tricesylphosphate. The phosphate esters are in general characterized by excellent fire resistant properties and high lubricity. However, their thermal stability is such that they are ordinarily unsuited for high temperature applications above about 300°F.

The synthetic base greases used in formulating the lubricant compositions formed by admixing a soap with an oil of any of the types described above. Such soaps are derived from animal or vegetable fats or fatty acids, wool grease, rosin or petroleum acids. Typical examples are lead oleate, lithium stearate, aluminium tristearate, calcium glycerides and sodium oleate. In addition, the polyester greases may contain unreacted fat, fatty acids, and alkali; unsaponifiable matter including glycerol and fatty alcohols; rosin or wool grease; water; and certain additives which may function as modifiers or peptizers.

In formulating our grease compositions, greases prepared by admixing a lithium soap with the polyester oils are preferred as they have superior oxidative stability as compared with greases formulated with other soaps, such as the sodium, calcium or lead soaps.

Our compositions are also excellent antioxidants for saturated hydrocarbon polymers such as polyethylene and polypropylene.

#### EXAMPLE 17

The benefits derived from the practice of this invention are demonstrated by comparative oxidation tests of uninhibited polyethylene and polyethylene containing an antioxidant of this invention. These tests are conducted as fol-

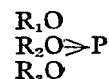
lows: The selected amount of antioxidant is blended with the polyethylene by milling a weighed quantity of plastic pellets on a warm roll-mill. The weighed quantity of antioxidant is added to the mill after the polyethylene has been premilled for a short period of time. The plastic containing the antioxidant is then added in weighed quantity to a standard size vessel and melted to give a surface of reproducible size. The vessel is then inserted into a chamber which may be sealed and which is connected to a capillary tube leading to a gas buret and levelling bulb. The apparatus is flushed with oxygen at room temperature, sealed, and the temperature is raised to 150°F. The oxygen pressure is maintained at 1 atmosphere by means of the levelling bulb. The oxygen uptake at the elevated temperature is recorded for the duration of the test. This procedure has been adopted since it has been found that many compounds may inhibit the oxidation for a certain induction period after which time a very sharp increase in the rate of oxygen uptake occurs indicating that the antioxidant has been exhausted. In tests of this nature 0.05 per cent 4,4'-methylenebis(2,6-diisopropyl phenol) was added to one sample of the polyethylene. Another sample of the polyethylene was tested uninhibited. A third sample contained 0.05 per cent 4,4'-methylenebis(2,6-diisopropyl phenol) and 0.0425 per cent bis(2-ethylhexyl) hydrogen phosphite. The induction period of the sample containing the 4,4'-methylenebis(2,6-diisopropyl phenol) was 32 hours, whereas the uninhibited sample had no induction period and took up oxygen immediately. After 20 hours of heating the uninhibited sample had absorbed over 45 ml. of oxygen.

The outstanding results obtainable with our antioxidant compositions in contrast to those obtained with the uninhibited polyethylene are demonstrated by the test which was conducted with our composition. When 0.05 per cent 4,4'-methylenebis(2,6-diisopropyl phenol) and 0.0425 per cent bis(2-ethylhexyl) hydrogen phosphite was compounded with the polyethylene, the induction period did not expire until 45 hours of heating at 150°C. That is to say the sample of polyethylene had absorbed essentially no oxygen until after 45 hours of heating. Thus, our compositions of this invention are outstandingly superior antioxidants for saturated hydrocarbon polymers.

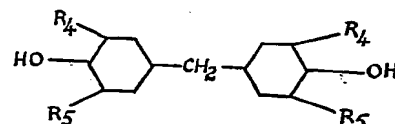
We are aware of the Public Health (Preservatives &c. in Food) Regulations, 1925—1953, and insofar as our invention relates to the manufacture for sale in the United Kingdom and/or sale in the United Kingdom of foodstuffs preserved by the process herein described, we make no claim to use the invention in contravention of the law.

**WHAT WE CLAIM IS:—**

1. A synergistic antioxidant mixture for addition to organic material subject to oxidative deterioration comprising a phosphite ester having the formula:



wherein  $R_1$  and  $R_2$  are alkyl, alkoxyalkyl, haloalkyl, cycloalkyl, halocycloalkyl, aralkyl, aryl, alkaryl, haloaryl, or haloalkaryl radicals and  $R_3$  is one of the aforementioned radicals or hydrogen; and a methylene bis-phenol having the formula:



wherein  $R_4$  is an alkyl group which contains from 3 to 12 carbon atoms and is branched on its alpha carbon atom and  $R_5$  is an alkyl group containing from 1 to 12 carbon atoms in amount such that there is from 0.005 to 1000 parts by weight of said phenol per part of phosphite.

2. Organic composition subject to oxidative deterioration containing a synergistic mixture according to claim 1, consisting of from 0.025 to 4 per cent by weight based on the material to be protected of the phosphite ester and from 0.01 to 5 per cent by weight based on the material to be protected of the methylene bis-phenol.

3. Organic lubricating composition according to claim 2, wherein said ester and said phenol are present in proportions such that there are from 0.5 to 5 moles of said ester per mole of said phenol.

4. Organic composition according to claim 2 or 3, wherein said ester is a dialkyl hydrogen phosphite in which each alkyl group contains up to 12 carbon atoms.

5. The organic composition according to claim 2, 3 or 4, wherein the organic material subject to oxidative deterioration is a solid saturated hydrocarbon polymer prepared by polymerization of a mono-olefinic hydrocarbon having from 2 to 5 carbon atoms.

6. The organic composition according to claim 2, 3 or 4, wherein the organic material subject to oxidative deterioration is a rubber-like, conjugated diolefin polymer.

7. Composition according to claim 2, wherein the organic material subject to oxidative deterioration is lubricating oil.

8. Organic composition according to claim 7, containing a synergistic mixture consisting of from 0.025 to 4 per cent by weight based on the oil of a dialkyl hydrogen phosphite in which each alkyl group contains from 1 to 8 carbon atoms and from 0.1 to 3 per cent by weight based on the oil of 4,4'-methylenebis-

(2,6-diisopropyl phenol) or 4,4'-methylenebis-(6-*tert*-butyl-*o*-cresol).

- 5 9. Organic composition according to claim 7, containing a synergistic mixture consisting of from 0.025 to 4 per cent by weight based on the oil of a dialkyl hydrogen phosphite in which each alkyl group contains from 4 to 12 carbon atoms and from 0.1 to 3 per cent by weight based on the oil of 4,4'-methylenebis-  
10 (2,6-di-*tert*-butyl phenol).

10. Organic material subject to oxidative deterioration containing antioxidant composition substantially as herein described.

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